

PHOTOPROTECTIVE/COSMETIC  
COMPOSITIONS COMPRISING  
DIBENZOYLMETHANE/TRIAZINE/DIPHENYLACRYLATE  
COMPOUNDS

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BACKGROUND OF THE INVENTION

Technical Field of the Invention:

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The present invention relates to novel cosmetic and/or dermatological compositions (hereinafter sometimes "antisun" or "sunscreen" compositions) for the photoprotection of the skin and/or the hair against UV radiation, in particular solar radiation. More especially, this invention relates to novel cosmetic and/or dermatological compositions exhibiting improved photostability and including, in a cosmetically and/or dermatologically acceptable substrate (vehicle, diluent or carrier), the combination of three specific screening agents.

The present invention also relates to the use of the subject compositions in the cosmetic and/or dermatological fields.

Description of the Prior Art:

It is known to this art that light radiation of wavelengths of from 280 nm to 400 nm permits the human epidermis to tan and that irradiation of wavelengths of from 280 nm to 320 nm, i.e., UV-B irradiation, causes erythemas and skin burns which can be harmful to the development of the natural tan; hence, this UV-B radiation must therefore be screened from the skin.

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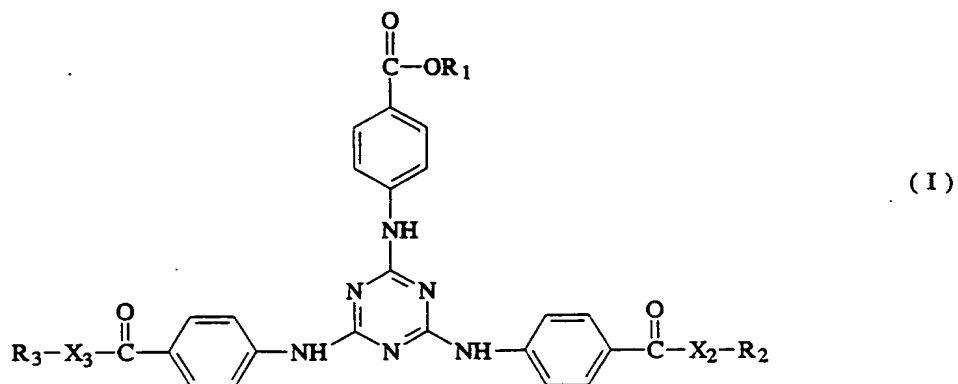
However, it has now been demonstrated that in the presence of 4-tert-butyl-4'-

5 methoxydibenzoylmethane and under UV irradiation, the  
aforesaid 1,3,5-triazine derivatives present the  
disadvantage of being extensively degraded chemically.  
Under these conditions, the combination of the two  
screening agents no longer provides a prolonged broad  
10 protection of the skin and of the hair against solar  
radiation.

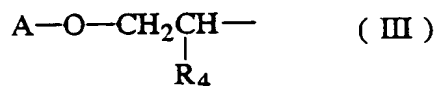
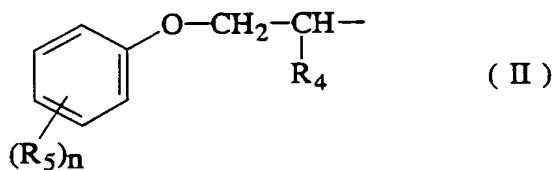
## SUMMARY OF THE INVENTION

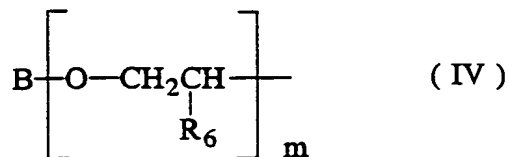
It has now unexpectedly been determined that the formulation of an alkyl  $\beta,\beta'$ -diphenylacrylate or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate into compositions containing 4-tert-butyl-4'-methoxydibenzoylmethane in combination with at least one 1,3,5-triazine derivative, and in particular with 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine, markedly enhances the stability of such at least one 1,3,5-triazine derivative within such compositions, and hence markedly enhances the overall effectiveness of these compositions.

Briefly, the present invention features novel cosmetic and/or dermatological compositions comprising, in a cosmetically and/or dermatologically acceptable carrier, diluent or vehicle, (i) 4-tert-butyl-4'-methoxydibenzoylmethane, (ii) at least one 1,3,5-triazine compound having the following structural formula (I):

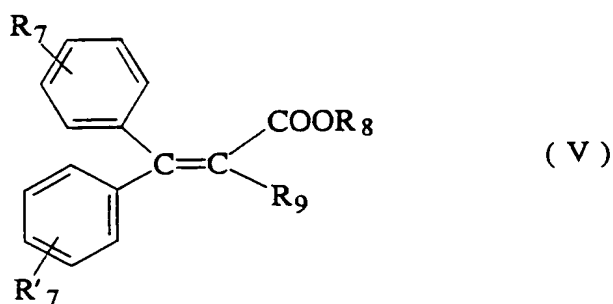


wherein  $X_2$  and  $X_3$ , which may be identical or different, are each an oxygen atom or the  $-NH-$  radical; and  $R_1$ ,  $R_2$  and  $R_3$ , which may be identical or different, are each a hydrogen atom, an alkali metal, an ammonium radical optionally substituted by one or more alkyl or hydroxyalkyl radicals, a linear or branched  $C_1-C_{18}$  alkyl radical, a  $C_5-C_{12}$  cycloalkyl radical optionally substituted by one or more  $C_1-C_4$  alkyl radicals, a polyoxyethylenated radical having from 1 to 6 ethylene oxide units and in which the terminal OH group is methylated, or a radical of the following formulae (II), (III) and (IV):





wherein  $R_4$  is hydrogen or a methyl radical,  $R_5$  is a  $C_1$ - $C_9$  alkyl radical,  $n$  is an integer ranging from 0 to 3,  $m$  is an integer ranging from 1 to 10, A is a  $C_4$ - $C_8$  alkyl radical or a  $C_5$ - $C_9$  cycloalkyl radical, B is a linear or branched  $C_1$ - $C_9$  alkyl radical, a  $C_5$ - $C_9$  cycloalkyl radical, or an aryl radical optionally substituted by one or more  $C_1$ - $C_4$  alkyl radicals, and  $R_6$  is hydrogen or a methyl radical, and (iii) at least one alkyl  $\beta,\beta'$ -diphenylacrylate or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate having the following structural formula (V):



in which R<sub>7</sub> and R'<sub>7</sub>, which may be identical or different, are in a meta- or para- position and are each a hydrogen atom, a straight or branched chain C<sub>1</sub>-C<sub>8</sub> alkoxy radical, or a straight or branched chain C<sub>1</sub>-C<sub>4</sub> alkyl radical; R<sub>8</sub> is a straight or branched chain C<sub>1</sub>-C<sub>12</sub> alkyl radical; and R<sub>9</sub> is a hydrogen atom or a -CN radical, with the proviso that said compositions are devoid of 2-ethylhexyl p-methoxycinnamate.

DETAILED DESCRIPTION OF BEST MODE AND  
SPECIFIC/PREFERRED EMBODIMENTS OF THE INVENTION

More particularly according to the present invention, cosmetic and/or dermatological compositions  
5 containing 4-tert-butyl-4'-methoxydibenzoylmethane in combination with at least one 1,3,5-triazine derivative are provided, in which compositions the concentration of 1,3,5-triazine compound remains relatively constant even if the compositions are  
10 subjected to the action of light.

Further, the alkyl  $\beta,\beta'$ -diphenylacrylates or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylates of the present invention present the advantage of possessing a good  
15 intrinsic screening power which contributes to the protection against UV irradiation conferred by the subject compositions and, in addition, the complete screening system [4-tert-butyl-4'-methoxydibenzoylmethane + 1,3,5-triazine derivative +  
20 (alkyl  $\beta,\beta'$ -diphenylacrylate or  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate)] exhibits overall a very good stability under the action of UV (photostability), which presents another advantage of the compositions according to the invention.

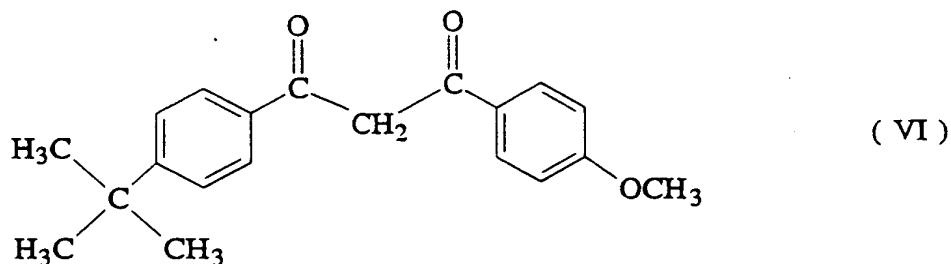
The present invention also features the use  
25 of an alkyl  $\beta,\beta'$ -diphenylacrylate or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate in, or for the formulation of, cosmetic and/or dermatological compositions containing 4-tert-butyl-4'-methoxydibenzoylmethane in combination with at least one 1,3,5-triazine compound as described  
30 above with a view to improving the stability to UV radiation (photostability) of said at least one 1,3,5-triazine compound in the subject compositions.

This invention also features a process for improving the stability to UV radiation

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(photostability) and, hence, the effectiveness of a cosmetic and/or dermatological composition comprising 4-tert-butyl-4'-methoxydibenzoylmethane and a 1,3,5-triazine compound as described above, in particular 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine, said process entailing incorporating into said composition an effective photostabilizing amount of an alkyl  $\beta,\beta'$ -diphenylacrylate or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate.

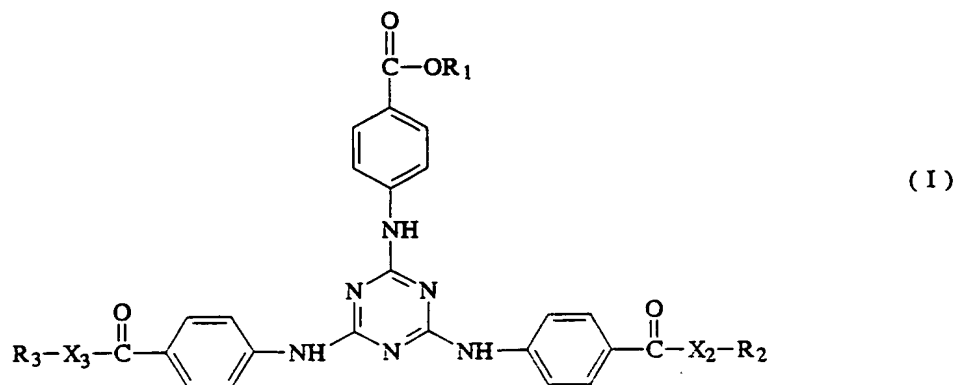
A first compound of the compositions according to the invention is, therefore, 4-tert-butyl-4'-methoxydibenzoylmethane. This compound is a screening agent which is per se well known and which has a high absorptivity in the UV-A region with a maximum at 358 nm. It is commercially available under the trademark of "Parsol 1789" by Givaudan and has the following structural formula (VI):



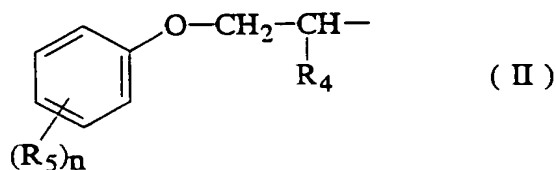
4-Tert-butyl-4'-methoxydibenzoylmethane is advantageously present in the compositions of the invention in an amount ranging from 0.2 % to 15 % by weight, relative to the total weight of the composition. This amount preferably ranges from 0.5 % to 10 %.

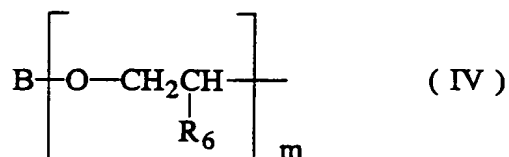
The second compound of the compositions of the present invention is a specific 1,3,5-triazine compound. The 1,3,5-triazine compounds of the present

invention are thus selected from among those having the following structural formula (I):



in which  $X_2$  and  $X_3$ , which may be identical or different, are each an oxygen atom or the -NH- radical; and  $R_1$ ,  $R_2$  and  $R_3$ , which may be identical or different, are each a hydrogen atom, an alkali metal, an ammonium radical optionally substituted by one or more alkyl or hydroxyalkyl radicals, a linear or branched  $C_1$ - $C_{18}$  alkyl radical, a  $C_5$ - $C_{12}$  cycloalkyl radical optionally substituted by one or more  $C_1$ - $C_4$  alkyl radicals, a polyoxyethylenated radical including from 1 to 6 ethylene oxide units and in which the terminal OH group is methylated, or a radical of the following formulae (II), (III) and (IV):





wherein  $\text{R}_4$  is hydrogen or a methyl radical,  $\text{R}_5$  is a  $\text{C}_1$ - $\text{C}_9$  alkyl radical,  $\underline{n}$  is an integer ranging from 0 to 3,  $\underline{m}$  is an integer ranging from 1 to 10, A is a  $\text{C}_4$ - $\text{C}_8$  alkyl radical or a  $\text{C}_5$ - $\text{C}_8$  cycloalkyl radical, B is a  
 5 linear or branched  $\text{C}_1$ - $\text{C}_8$  alkyl radical, a  $\text{C}_5$ - $\text{C}_8$  cycloalkyl radical or an aryl radical optionally substituted by one or more  $\text{C}_1$ - $\text{C}_4$  alkyl radicals, and  $\text{R}_6$  is hydrogen or a methyl radical.

A first, more particularly preferred class  
 10 of 1,3,5-triazine compounds is that especially described in EP-A-0 517 104, of the 1,3,5-triazines having the above formula (I) and exhibiting all of the following characteristics:

$\text{X}_2$  and  $\text{X}_3$  are identical and are each an oxygen atom  
 15  $\text{R}_1$  is a  $\text{C}_5$ - $\text{C}_{12}$  cycloalkyl radical optionally substituted by one or more  $\text{C}_1$ - $\text{C}_4$  alkyl radicals, or a radical of formula (II), (III) or (IV) above, in which:

B is a  $\text{C}_1$ - $\text{C}_4$  alkyl radical,

20  $\text{R}_6$  is the methyl radical,

$\text{R}_2$  and  $\text{R}_3$ , which may be identical or different, are each hydrogen, an alkali metal, an ammonium radical optionally substituted by one or more alkyl or hydroxyalkyl radicals, a linear or branched  $\text{C}_1$ - $\text{C}_{18}$

B is a C<sub>1</sub>-C<sub>4</sub> alkyl radical,  
R<sub>6</sub> is the methyl radical.

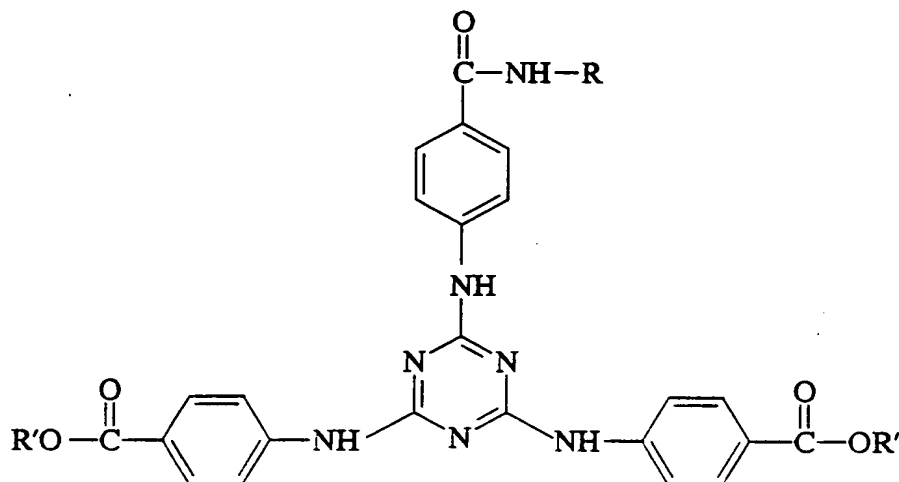
A second preferred class of 1,3,5-triazine compounds according to the invention is that especially described in EP-A-0 570 838, of the 1,3,5-triazines having the formula (I) and exhibiting the combination of the following characteristics:

X<sub>3</sub> is the -NH- radical,  
R<sub>3</sub> is a linear or branched C<sub>1</sub>-C<sub>18</sub> alkyl radical, or a C<sub>5</sub>-C<sub>12</sub> cycloalkyl radical optionally substituted by one or more C<sub>1</sub>-C<sub>4</sub> alkyl radicals,

R<sub>1</sub> is hydrogen, an alkali metal, an ammonium radical, a radical of formula (IV), a linear or branched C<sub>1</sub>-C<sub>18</sub> alkyl radical or a C<sub>5</sub>-C<sub>12</sub> cycloalkyl radical optionally substituted by one or more C<sub>1</sub>-C<sub>4</sub> alkyl radicals, with the provisos that:

if X<sub>2</sub> is the -NH- radical, then R<sub>2</sub> is a linear or branched C<sub>1</sub>-C<sub>18</sub> alkyl radical or a C<sub>5</sub>-C<sub>12</sub> cycloalkyl radical optionally substituted by one or more C<sub>1</sub>-C<sub>4</sub> alkyl radicals, and  
if X<sub>2</sub> is oxygen, then R<sub>2</sub> is hydrogen, an alkali metal, an ammonium radical, a radical of formula (IV), a linear or branched C<sub>1</sub>-C<sub>18</sub> alkyl radical or a C<sub>5</sub>-C<sub>12</sub> cycloalkyl radical optionally substituted by one or more C<sub>1</sub>-C<sub>4</sub> alkyl radicals.

A particularly preferred 1,3,5-triazine of this second class is that having the following structural formula:



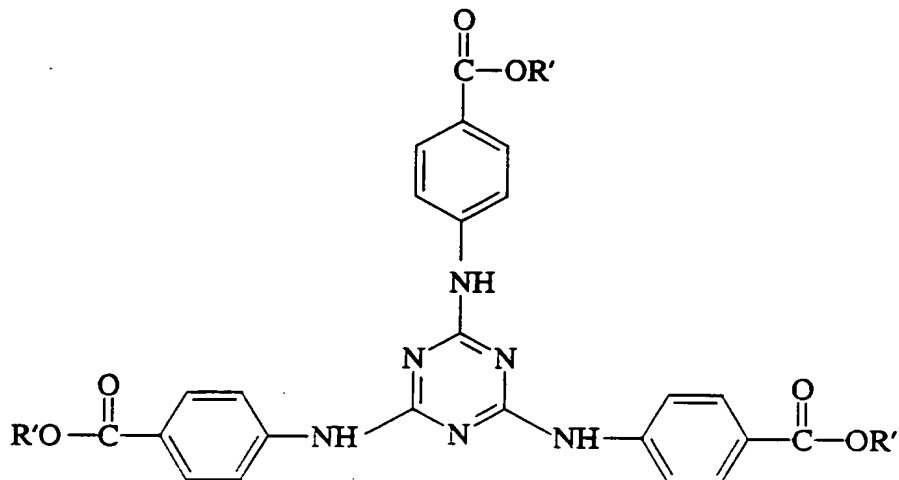
in which R' is a 2-ethylhexyl radical and R is a tert-butyl radical.

A third preferred class of compounds is that especially described in U. S. Patent No. 4,724,137, of 1,3,5-triazines having the formula (I) and exhibiting all of the following characteristics:

X<sub>2</sub> and X<sub>3</sub> are identical and are each an oxygen atom,

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical and are each a C<sub>6</sub>-C<sub>12</sub> alkyl radical or a polyoxyethylene radical having from 1 to 6 ethylene oxide units and in which the terminal OH group is methylated.

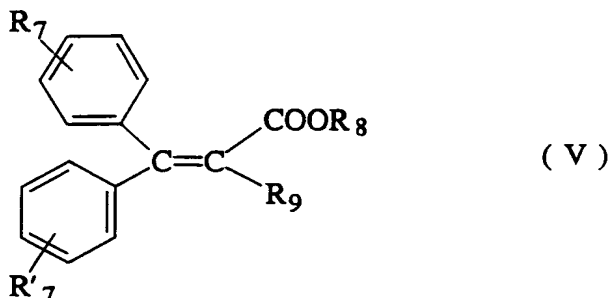
A particularly preferred 1,3,5-triazine of this third class is 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine, which is a screening agent per se known to this art, which is active in the UV-B region, which is in a solid form and which is commercially available under the trademark "Uvinul T 150" by BASF. This compound has the following structural formula:



in which R' is a 2-ethylhexyl radical.

The 1,3,5-triazine derivative(s) is (are) generally present in the compositions of the invention in an amount that can range from 0.5 % to 20 %, preferably from 1 % to 10 % by weight, relative to the total weight of the composition.

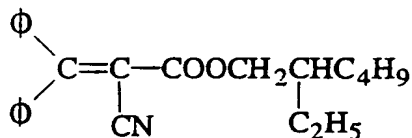
A third, absolutely essential, compound of the compositions according to the invention is a compound of the class including alkyl  $\beta,\beta'$ -diphenylacrylates and alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylates. The alkyl  $\beta,\beta'$ -diphenylacrylates and alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylates according to the present invention are selected from among those having the following structural formula (V):



in which  $R_7$  and  $R'_7$ , which may be identical or different, are in a meta- or para- position and are each hydrogen, a straight or branched chain  $C_1-C_9$  alkoxy, or a straight or branched chain  $C_1-C_4$  alkyl radical,  $R_8$  is a straight or branched chain  $C_1-C_{12}$  alkyl radical, and  $R_9$  is a hydrogen atom or a  $-CN$  radical.

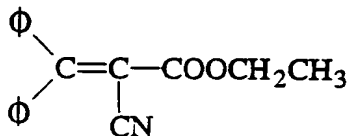
Among the alkyl  $\beta, \beta'$ -diphenylacrylates and alkyl  $\alpha$ -cyano- $\beta, \beta'$ -diphenylacrylates according to the present invention, more particularly preferred are 2-ethylhexyl  $\alpha$ -cyano- $\beta, \beta'$ -diphenylacrylate and ethyl  $\alpha$ -cyano- $\beta, \beta'$ -diphenylacrylate.

2-Ethylhexyl  $\alpha$ -cyano- $\beta, \beta'$ -diphenylacrylate, also designated octocrylene, is a known lipophilic screening agent absorbing in the UV-B region. It is available commercially and marketed under the trademark "Uvinul N 539" by BASF. It has the following structural formula:



in which  $\phi$  denotes a phenyl radical.

Ethyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate, also designated etocrylene, is also a liposoluble screening agent, absorbing in the UV-B region. It is available commercially and marketed under the trademark "Uvinul N 35" by BASF. It has to the following structural formula:



in which  $\phi$  denotes a phenyl radical.

Thus, when an alkyl  $\beta,\beta'$ -diphenylacrylate or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate is added in sufficient quantity to an antison or sunscreen composition containing 4-tert-butyl-4'-methoxydibenzoylmethane and a 1,3,5-triazine derivative as described above, an increase in the stability of said 1,3,5-triazine derivative to light is observed and, hence, an improvement in the effectiveness of the photoprotecting composition over the course of time.

The alkyl  $\beta,\beta'$ -diphenylacrylate or alkyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate is preferably present in the compositions according to the invention in an amount of at least 0.5 % by weight, relative to the total weight of the composition. This amount also preferably ranges from 0.5 % to 20 % by weight, relative to the total weight of the composition.

The cosmetic and/or dermatological compositions of the present invention may, of course, contain one or several additional sunscreens which are active in the UV-A and/or UV-B region (absorbers) which are hydrophilic or lipophilic, other, naturally,

than the three screening agents indicated above.

These additional screening agents are advantageously selected from among cinnamic compounds, salicylic compounds, benzylidene camphor compounds,

5 benzimidazole compounds, triazine compounds other than those indicated above, benzophenone compounds,  $\beta, \beta'$ -diphenylacrylate compounds other than those indicated above, p-aminobenzoic acid compounds and the polymer screening agents and silicone screening agents  
10 described in WO-93/04665. Other examples of organic screening agents are provided in EP-A 0,487,404.

The compositions according to the invention preferably do not contain 2-ethylhexyl p-methoxycinnamate. Indeed, 2-ethylhexyl p-methoxycinnamate  
15 can destabilize compositions comprising 4-tert-butyl-4'-methoxydibenzoylmethane and a 1,3,5-triazine compound, such as the subject compositions.

The compositions of this invention may also contain agents for artificial tanning and/or darkening  
20 of the skin (self-tanning agents), such as, for example, dihydroxyacetone (DHA).

The cosmetic and/or dermatological compositions of the invention may further contain pigments or nanopigments (primary particle mean size  
25 generally ranging from 5 nm to 100 nm, preferably from 10 to 50 nm) of coated or uncoated metal oxides such as, for example, nanopigments of oxide of titanium (amorphous or crystalline in rutile and/or anatase form), of iron, of zinc, of zirconium or of cerium,  
30 which are all photoprotective agents which are per se well known to this art, acting by physical blocking (reflection and/or scattering) of UV radiation. Conventional coating agents are, furthermore, alumina and/or aluminum stearate. Such coated or uncoated

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The lower alcohols and polyols are  
5 representative of the organic solvents.

One skilled in this art will, of course, take care to select the aforementioned additional optional compound(s) (in particular the additional screening agents) and/or their amounts such that the advantageous properties inherent in the ternary association in accordance with the invention are not, or are substantially not, adversely affected by the envisaged incorporation(s).

The subject compositions may be formulated in the form of an emulsion, simple or complex (O/W, W/O, O/W/O or W/O/W) such as a cream, a milk, an ointment, or in the form of a gel or of a cream gel, of powder, of solid stick and optionally may be packaged as an aerosol and be in the form of a mousse or spray.

When an emulsion, the aqueous phase thereof may include a nonionic vesicular dispersion prepared according to known techniques (Bangham, Standish and



water-in-oil emulsions, nonionic vesicular dispersions or suspensions.

By way of example, in the case of  
antisun/sunscreen formulations in accordance with the  
5 invention which comprise a carrier of the oil-in-water  
emulsion type, the aqueous phase (including,  
especially, the hydrophilic screening agents)  
generally constitutes from 50 % to 95 % by weight,  
preferably from 70 % to 90 % by weight, relative to  
10 the combined formulation, the oily phase (including,  
especially, the lipophilic screening agents) from 5 %  
to 50 % by weight, preferably from 10 % to 30 % by  
weight, relative to the combined formulation, and the  
(co)emulsifier(s) constitute from 0.5 % to 20 % by  
15 weight, preferably from 2 % to 10 % by weight,  
relative to the combined formulation.

The present invention thus also features a  
cosmetic treatment regime for protecting the skin  
and/or the hair against UV radiation, in particular  
20 solar radiation, comprising topically applying thereto  
an effective photoprotecting amount of a cosmetic  
composition as described above.

In order to further illustrate the present  
invention and the advantages thereof, the following  
25 specific examples are given, it being understood that  
same are intended only as illustrative and in nowise  
limitative.

#### EXAMPLES:

Four oil-in-water emulsions A, B, C and D  
30 were produced, in which the common carrier had the  
following composition (the quantities are expressed in

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% of weight relative to the total weight of the composition):

5	(a) 80/20 mixture of cetylstearyl alcohol and of oxyethylenated cetylstearyl alcohol (33 EO) marketed under the trademark "Dehsconet 390" by Tensia			7 %
	(b) mixture of glycerol mono- and distearate marketed under the trademark "Cerasynth SD" by ISP			2 %
10	(c) cetyl alcohol			1.5 %
	(d) polydimethylsiloxanes marketed under the trademark "DC 200 Fluid" by Dow Corning			1.5 %
15	(e) benzoate of C <sub>12</sub> /C <sub>15</sub> alcohols, marketed under the trademark "Finsolve TN" by Finetex			15 %
	(f) ethylenediaminetetraacetic acid disodium salt, 2 H <sub>2</sub> O			0.1 %
	(g) glycerin			20 %
20	(h) stabilizers			q.s.
	(i) demineralized water			q.s. 100 %

The emulsion A (comparative) additionally included a 1,3,5-triazine compound which was 2,4,6-tris[p-(2'-ethylhexyl)-1'oxycarbonyl]anilino]-1,3,5-triazine (Uvinul T 150). Emulsion B, also comparative, contained Uvinul T 150 in combination with 4-tert-butyl-4'-methoxydibenzoylmethane (Parsol 1789). Emulsion C, according to the invention, included, besides Uvinul T 150 and Parsol 1789, 2-ethylhexyl  $\alpha$ -cyano- $\beta,\beta'$ -diphenylacrylate (Uvinul N 539). Emulsion D, comparative, contained Uvinul T 150 in combination with Parsol 1789, but with a

conventional UV-B screening agent which was octyl methoxycinnamate (Parsol MCX).

The compositions of the emulsions A, B, C and D with regard to the various screening agents indicated above which they contained, are reported in Table I below (the quantities are expressed as weight % relative to the total weight of the composition):

**TABLE (I):**

Screening agent	Emulsion A (comparative)	Emulsion B (comparative)	Emulsion C (invention)	Emulsion D (comparative)
Uvinul T 150	1.5 %	1.5 %	1.5 %	1.5 %
Parsol 1789	-	0.5 %	0.5 %	0.5 %
Uvinul N 539	-	-	10 %	-
Parsol MCX	-	-	-	10 %

In the case of each of these emulsions, the percentage of residual 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine was determined after irradiation with UV according to the following procedure: four control samples and four test samples were prepared in the case of each formulation. 16 mg of formulation, which was spread over an area of 2 cm x 4 cm, were deposited on depolished PMMA (polymethyl methacrylate) panels rinsed beforehand with water and then dried. The panels were then irradiated (Heraeus Suntest CPS) for 4 hours in a chamber where the temperature was controlled in the region of 35°-40°C in order to simulate a natural UV irradiation, the control panels being stored in the dark during the period of irradiation of the other panels.

The samples were next treated in the following manner: the screening agents were extracted

by immersing each panel in 55 ml of isopropanol in order to dissolve the screening agents. The panels and the solvent containing the screening agents were next treated with ultrasonics for 5 minutes to ensure an efficient extraction. The solutions obtained were analyzed by high performance liquid-phase chromatography.

For each formula tested, the residual proportion of 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine after irradiation was determined by the ratio of its concentration in the irradiated sample to its concentration in the unirradiated sample.

The results, as percentage of remaining 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine, are reported in the following Table II:

TABLE (II):

Emulsion	Residual Uvinul T 150
Emulsion A (comparative)	80 %
Emulsion B (comparative)	68 %
Emulsion C (invention)	99 %
Emulsion D (comparative)	79 %

While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof.

5 Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims, including equivalents thereof.

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